(2)

STUDY OF

SELF-PROPAGATING CONDENSED

PHASE REACTIONS - $TiB_2$ SYNTHESIS

FINAL REPORT

BY

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Delta H sub f deg. + or -

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This effort was undertaken to investigate the basic aspects of the condensed phase titanium-boron reaction leading to the formation of high density and quality $TiB_2$ under self-propagating conditions. Candidate factors for controlling microstructure were addressed and were utilized as variables in series of runs which produced $TiB_2$.

The heat of formation of $TiB_2$ was measured directly from the reacting elements in a modified bomb calorimeter; a $\Delta H^{\circ}_{f,298} = -71.81 \pm 1.9$ was

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) determined which is sufficient to produce liquid $TiB_2$ under adiabatic conditions.

Variations of stoichiometry and particle size of starting powders resulted in microstructure and density differences in the final $TiB_2$ product.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

## LIST OF TABLES

## I. INTRODUCTION

The use of self-propagating reactions in forming high purity refractory compounds has been explored by the Soviets over a period of several years with some success in forming cost effective abrasive powders. The formation of a densified shape of $TiB_2$ by applying only pressure during the exothermic self-propagating reaction was first demonstrated by Zavitsanos and Morris(1) where $TiB_2$ discs were formulated with a density of 96.7% theoretical.

The advantages of self-propagating processes can be many including higher purity, strength, toughness and perhaps production cost. This program was undertaken in an effort to investigate the fundamental aspects of the self-propagating reaction between Ti and B powders leading to the highly exothermic formation of $TiB_2$, i.e. $Ti(c) + 2B(c) \rightarrow TiB_2(c) + \Delta H$.

The objective of the program was to identify the mechanism of the reaction and identify the most promising conditions leading to highest purity, density and toughness; the suggested candidate factors controlling microstructure and density are the following:

1. Starting reactant powders: purity and size distribution.
2. Powder mixing: ratio, uniformity, seeding.
3. Reaction initiation: point source (hot wire at 900°C); volume heating by furnace to 900°C.
4. Pressure: magnitude and method of application.

(1) "Synthesis of Titanium Diboride by a Self-Propagating Reaction," by P.D. Zavitsanos and J.R. Morris, Jr., Ceramic Eng. and Sci. Proc., July-August 1983, pp. 624-633.

## II. EXPERIMENTAL INVESTIGATION

### A. Heat of Reaction Measurements by Bomb Calorimetry

The heat of formation of $TiB_2$ as reported in the JANAF Tables[(2)] is in serious dispute with values ranging from -50 $\pm$ 5 kcal/mole to 73.6 $\pm$ 4.5 kcal/mole. The significance of this problem in the self-propagation synthesis technique is that the lower value of the heat of formation would not be sufficient to produce a liquid $TiB_2$ product which may play a key role in the densification step. For this reason it was considered necessary to measure the heat of formation by a "direct" method as compared to the JANAF values which were all "indirect."

An automatic adiabatic Bomb Calorimeter (Parr Instrument Co. Model 1291) was used to measure the heat of the reaction $Ti + 2B \rightarrow TiB_2 + \Delta H$. An attempt was also made to measure $2Ti + B_4C \rightarrow 2TiB_2 + C$ but this was not possible under the existing experimental conditions. However the $\Delta H$ of several Ti/2B, $2Ti/B_4C$ mixtures was possible to be measured.

The Parr bomb calorimeter consists of a sealed stainless steel reaction vessel ("bomb") immersed in a constant temperature water bath. The bomb is equipped with two electrical feedthroughs, a valve to pressurize the bomb, and a vent valve. Reactants are held in a small steel cup suspended in the bomb. A thin fusible wire above the cup is connected to the electrical feed posts. A power supply attached to these posts serves to melt the fuse wire onto the reactants and thus trigger the exothermic reaction. The resulting temperature increase is used to calculate the $\Delta H$ for the reaction. A system calibration provides the necessary conversion calories/degree temperature

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(2) JANAF Thermochemical Data, Dow Chemical Company, Midland, Michigan

rise. The calibration is determined from a standard material of known heat output (Benzoic Acid).

The Ti/B reaction was studied under several conditions of applied atmosphere (air and $N_2$) using two sources of boron, elemental B and $B_4C$. Further details of experimental conditions and the resulting heat ( $H^{\circ}_{f,298}$) are shown in Table I. The results suggest the reaction is so fast that surface heterogeneous reaction(s) with oxygen and/or nitrogen play an insignificant role in the observed heat release which is 1,033 cal/g (or 71.81 kcal/mole) for the Ti/2B mixture and considerably less when the source of boron is $B_4C$ instead of B.

Table II shows the results of this work in comparison with all the JANAF values, and supports the view that an adequate amount of energy is released to raise the (adiabatic) temperature of the product above the melting point of $TiB_2$ which is 3,003°K.

B. Reactant Powder Evaluation

The evaluation of the powders used in the study of titanium diboride synthesis by self-propagating reaction was done by mass spectrometry on individual powder samples and by SEM/energy dispersive x-ray microanalysis (SEM/EDX) on individual powders and on unreacted powder mixes of Ti and B.

1. Mass Spectrometry

Time of flight mass spectrometric measurements were made on volatile products from two sources of boron (Callery and Atlantic Equipment Engineers (AEE)) and two sources of titanium (AEE and Alfa Products). This was done to detect any significant adsorbates or impurities between sources of the two powder materials used to fabricate $TiB_2$ that might account for

## TABLE I

## PARR BOMB HEAT OF REACTION DATA SUMMARY

| SAMPLE COMPOSITION $Ti + 2B$ | $2Ti + B_4C$ | | SAMPLE WT. (g) | $\Delta H^{\circ}_{f,298}$ (cal/g) | ATMOSPHERE |
|---|---|---|---|---|---|
| 100% (WT) | --- | POWDER | 5.49 | 1087 | AIR + $N_2$* |
| 100 | --- | PELLET | 5.70 | 1037 | $N_2$+ |
| 100 | --- | POWDER | 4.38 | 994 | $N_2$+ |
| 100 | --- | POWDER$^{\Delta}$ | 6.06 | 1004 | $N_2$+ |
| 100 | --- | POWDER$^{\Delta}$ | 5.97 | 1044<br>1033 AVG | $N_2$+ |
| 70 | 30 | POWDER | 4.85 | 854 | $N_2$+ |
| 50 | 50 | POWDER | 5.93 | 744 } 764 AVG | $N_2$+ |
| 50 | 50 | POWDER$^{\Delta}$ | 5.91 | 784 } | $N_2$+ |
| -- | 100 | DID NOT IGNITE | | | $N_2$+ |

* AMBIENT AIR IN BOMB PRESSURIZED TO 20 PSIG WITH $N_2$

\+ PARR BOMB PURGED WITH $N_2$ THEN PRESSURIZED TO 20 PSIG

$\Delta$ PREPARED FROM BALL MILLED POWDERS

## TABLE II

## THERMOCHEMISTRY

$$Ti(s) + 2B(s) \longrightarrow TiB_2(s) = \Delta H$$

| $\Delta H^{\circ}_{f,298}$ (kcal/mole) | SOURCE | METHOD |
|---|---|---|
| $-66.85 \pm 2.7$ | JANAF | INDIRECT |
| $-50 \pm 5$ | " | " |
| $-73.6 \pm 4.5$ | " | " |
| $-63.6 \pm 2.0$ | " | " |
| $-67.5 \pm 3.5$ | " | " |
| | | |
| $71.81 \pm 1.9$ | THIS WORK | DIRECT BOMB CALORIMETRY |

differences in behavior during formation. Both titanium samples showed hydrogen evolving above about 1600°C, while the Alfa material showed somewhat more carbon and oxygen species as well as a higher total volatile content as evident by the total mass spectrometer signal.

Both boron specimens gave identical responses relative to mass number, but the Callery specimen gave about 30% more total counts due mainly to mass numbers 44 and 45. A summary of data is given in Table III. Inasmuch as the prior history of the materials as well as the processes by which they were made are not completely known, it is not possible to assign chemical compound formulas to all mass numbers observed in the analyses. Yet some possibilities are listed in Table III mainly resulting from the presence of carbon, oxygen, hydrogen and/or water vapor adsorbed on the powder surfaces.

2. SEM/EDX Evaluation

The suppliers and the powder descriptions are shown in Table IV; this table also shows the figure numbers for the powders examined by SEM/EDX methods. Figures 1 and 2 illustrate the powder morphology for AEE -325 mesh Ti and for AEE -325 mesh B; this powder combination, in stoichiometric (Ti+2B) and 7.5 weight percent excess Ti (1.077 Ti + 2B) formulas was found to obtain consistent density and strength properties when made into densified reaction pressings.

The powder mixes, shown as green compact fracture surfaces in Figures 3 to 8, represent various combinations of four boron powder sizes (-60 mesh, -325 mesh, sub-micron, and 320 angstroms) with two titanium powders (-325 mesh and 1-5 micron).

## TABLE III

## SUMMARY OF MASS SPECTROMETRY RESULTS, TOTAL COUNTS TO 1800°C

| | | TITANIUM POWDERS | | | BORON POWDERS | |
|---|---|---|---|---|---|---|
| MASS NO. | POSSIBLE SPECIES | AEE Ti | ALFA Ti | POSSIBLE SPECIES | CALLERY B | AEE B |
| 1 | H | | 370 | | | |
| 2 | $H_2$ | 7640 | 7730 | $H_2$ | 1350 | 760 |
| 11 | | | | B | 480 | 200 |
| 12 | C | | 10620 | B H, | 200 | 590 |
| 15 | $CH_3$ | | 5250 | | | |
| 16 | O | 1300 | 9890 | | | |
| 20 | -- | 3750 | | -- | 2770 | 2360 |
| 36 | -- | 1070 | | -- | 3130 | 150 |
| 44 | $CO_2$ | 3250 | | $CO_2$ | 6010 | 1950 |
| 45 | | | | $H_2B\ O_2$ | 4250 | 2550 |
| 47 | | | | -- | 5090 | 6900 |
| 48 | Ti | 3100 | 5250 | | | |
| 49 | | | | -- | 3350 | 5020 |
| 65 | | | | -- | | 600 |
| 83 | | | | -- | 250 | |
| TOTAL (COUNTS) | | 20110 | 38740 | | 26880 | 21080 |

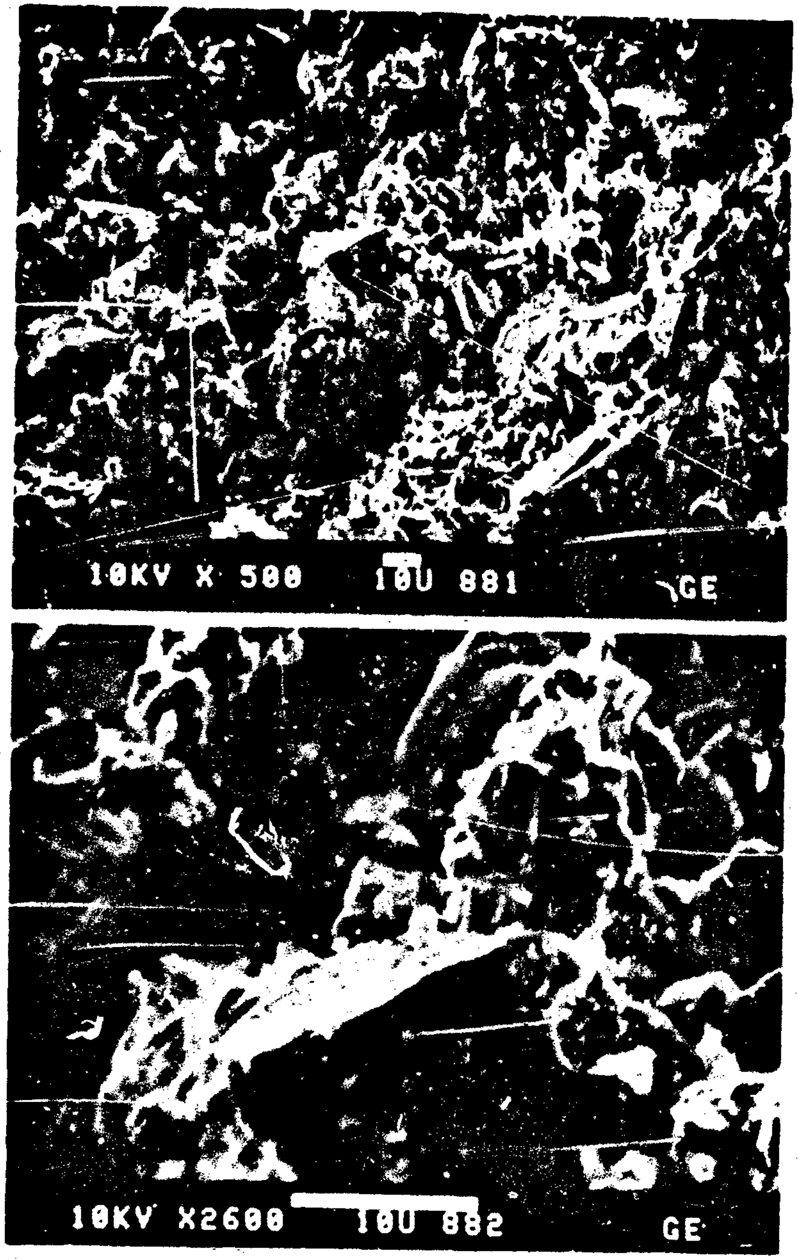
TABLE IV

SUPPLIER POWDER DESCRIPTION

| MATERIAL | SUPPLIER POWDER DESCRIPTION | SUPPLIER[1] | SEM/EDX EXAMINATION |
|---|---|---|---|
| TITANIUM | -325 MESH; 99% METAL PURITY; PACKED UNDER ARGON | ALFA | ALFA -325 Ti + CALLERY SUB-MICRON B; (FIGURE 8 ) |
| | -325 MESH; 99.7% | AEE | AEE -325 Ti (FIGURE 1 ); AEE -325 Ti + AEE -325 B (FIGURE 2 ) |
| | 1-5 MICRON; 99.7% | AEE | AEE 1-5 Ti + AEE -325 B (FIGURE 4 ) |
| BORON | -60 MESH CRYSTALLINE; 99.7% METAL PURITY, 99.4% TOTAL PURITY | ALFA | ALFA -60 B + AEE -325 Ti (FIGURE 6 ) |
| | -325 MESH CRYSTALLINE; 99.5% MIN. PURITY | AEE | AEE -325 B (FIGURE 2 ); AEE -325 B + AEE -325 Ti (FIGURE 3 ) |
| | SUB-MICRON, HIGH PURITY; 99.9% | CALLERY | CALLERY SUB-MICRON B + ALFA -325 Ti (FIGURE 8 ) |
| | 320 ANGSTROM; PACKED UNDER NITROGEN | CALLERY | CALLERY 320 B + AEE 1-5 Ti (FIGURE 7 ) |
| BORON CARBIDE | 1-5 MICRON; 99.7% | AEE | NONE |
| TITANIUM DIBORIDE | 1-5 MICRON; 99.8% | AEE | NONE |

(1) ALFA = ALFA PRODUCTS, DANVERS, MASSACHUSETTS
AEE = ATLANTIC EQUIPMENT ENGINEERS, BERGENFIELD, NEW JERSEY
CALLERY = CALLERY CHEMICAL CO., CALLERY, PENNSYLVANIA


Figure 1. SEM examination of AEE -325 mesh Titanium from two different powder lots.



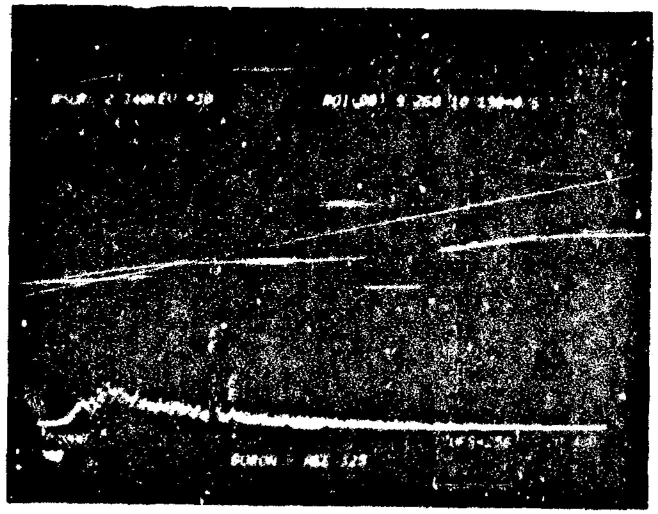



Figure 2 . SEM/EDX examination of AEE -325 mesh boron.

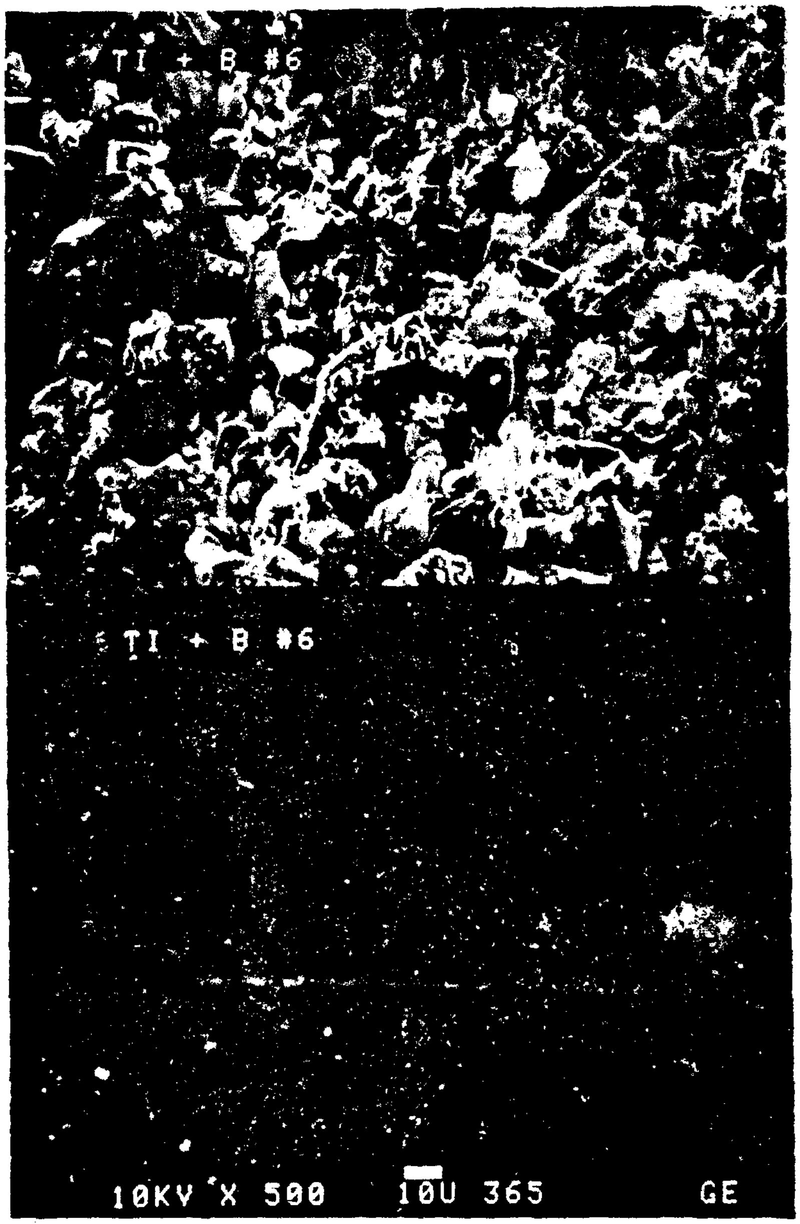
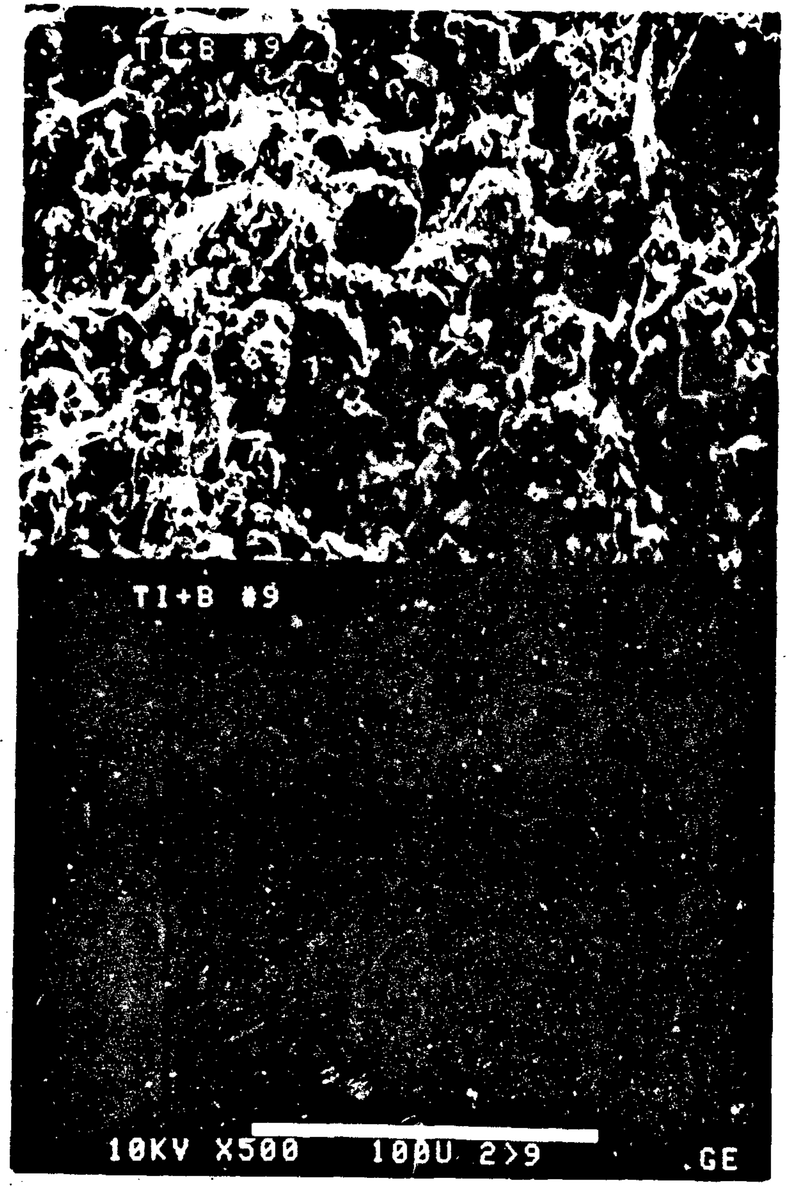



Figure 3. Fracture surface of green compact of Ti + B Mix #6 stoichiometric Ti + 2B, AEE -325 mesh titanium + AEE -325 mesh boron. Top, SEM photomicrograph of particle shapes and sizes. Bottom, Ti x-ray map of same area.



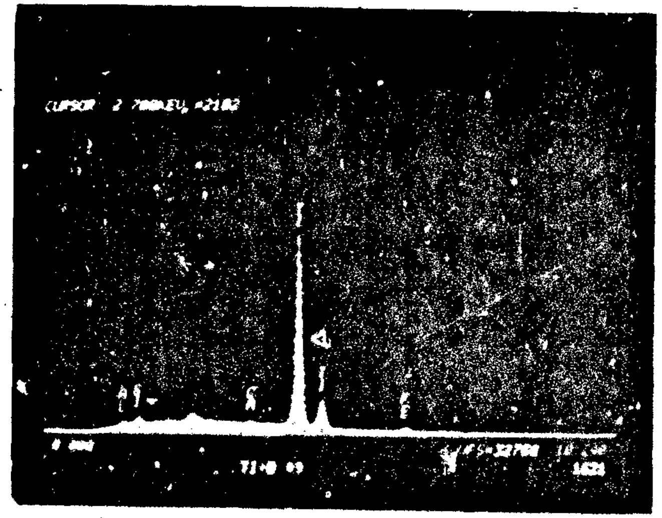



Figure 4. SEM/EDX examination of green compact of stoichiometric T + 2B, AEE 1-5 micron titanium + AEE -325 mesh boron.
Left: SEM image and titanium x-ray map of identical areas.
Top: X-ray energy spectra of powder mix.

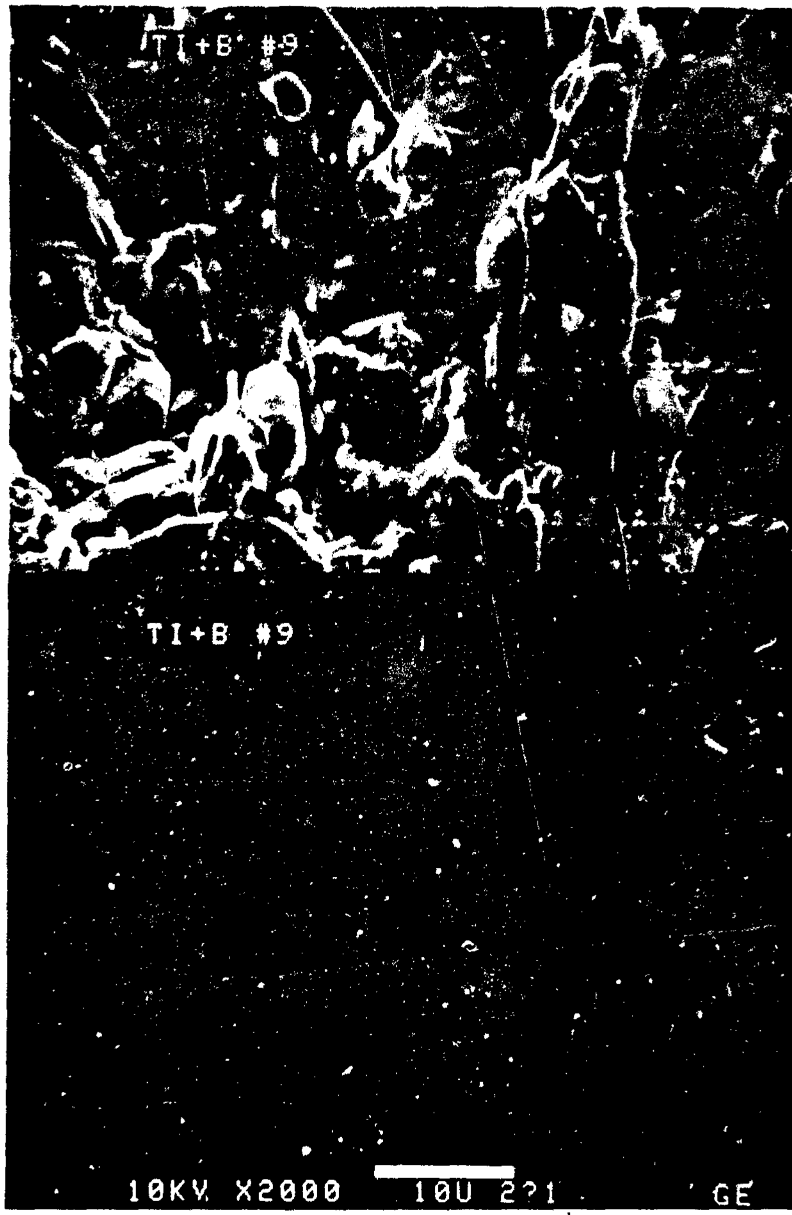
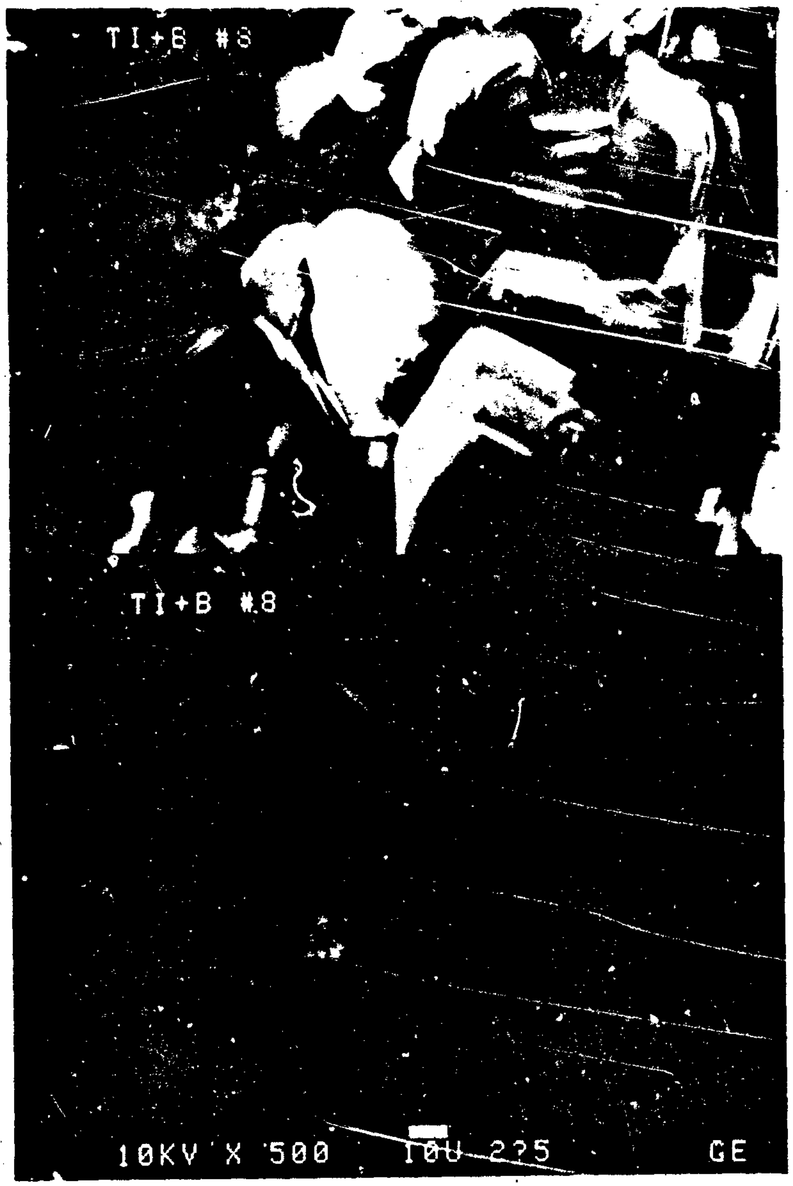



Figure 5 . SEM examination of green compact of stoichiometric Ti + 2B, AEE 1-5 micron titanium + AEE -325 mesh boron. Top: SEM image; Bottom; Titanium x-ray map of identical area.


Figure 6 . Fracture surface of green compact of stoichiometric Ti + 2B, AEE -325 mesh titanium + Alfa -60 mesh boron. Top: SEM photomicrograph illustrating particle shapes and sizes. Bottom: Ti x-ray map of same area.



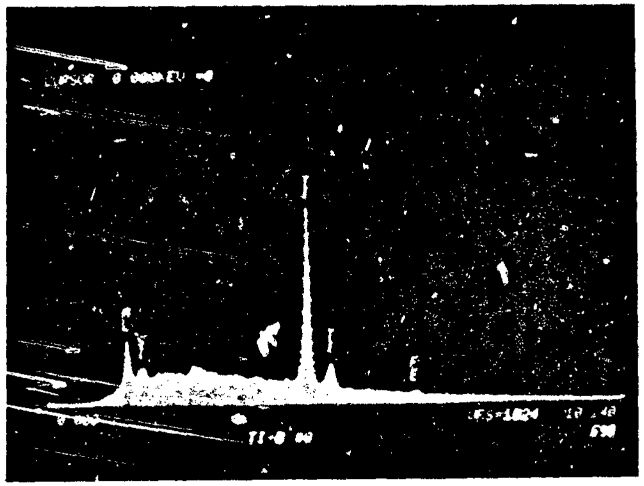



Figure 7. SEM/EDX examination of green compact fracture of stoichiometric Ti + 2B, AEE 1-5 micron titanium + Callery 320Å boron.
Left: Detail of powder particle morphology and agglomeration with Ti x-ray of same area.
Top: X-ray spectra of powder mix.

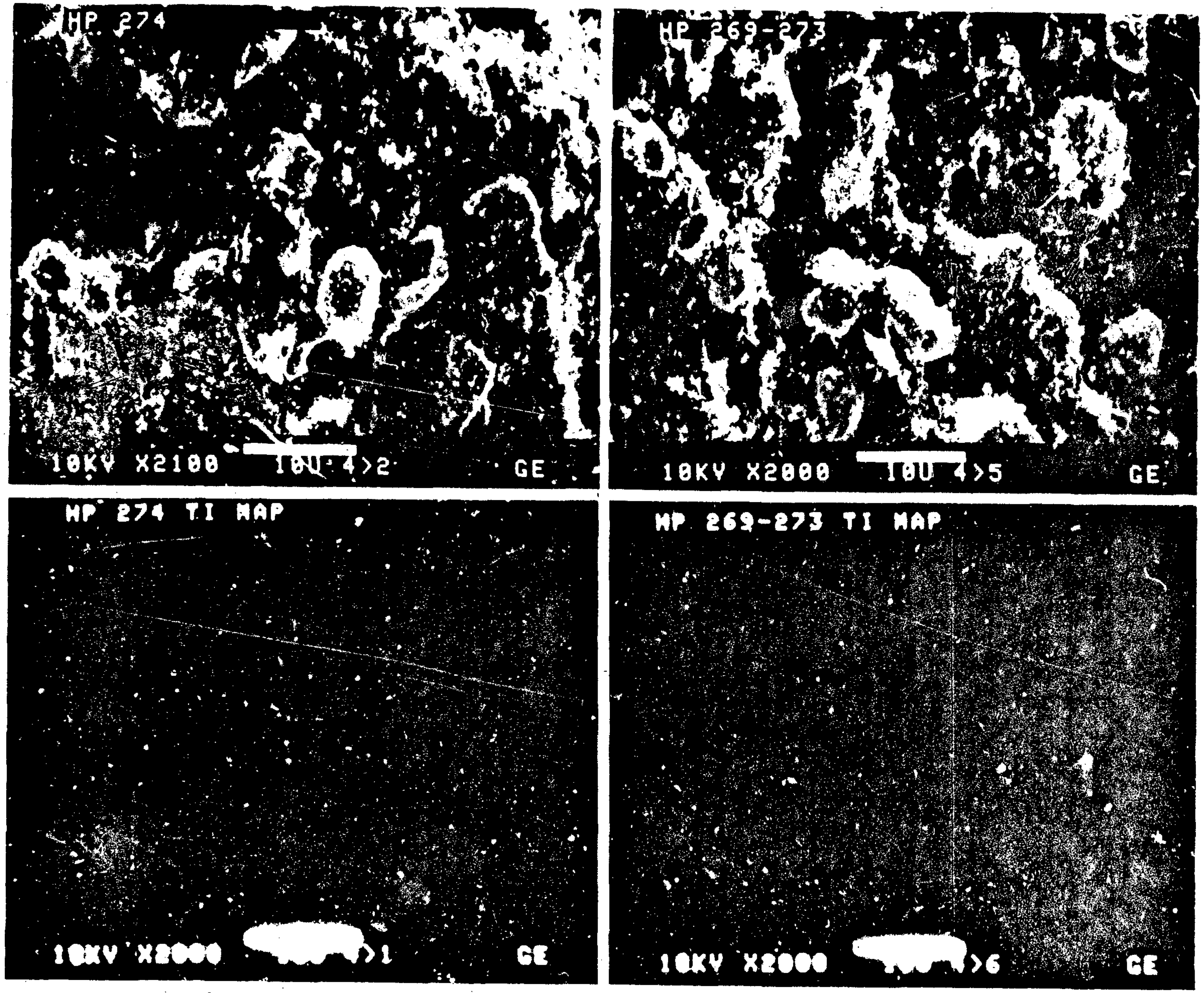



Figure 8. SEM examination of powder mix: Alfa -325 mesh Titanium + Callery Sub-micron Boron. (This combination resulted in uncontrolled reaction during pressing.)

The Callery boron, originally identified by Callery Chemical Co. as "320 angstrom" mean particle size was an in-house supply used in early experimentation. Figure 7 indicates that the powder had a thin lamellae morphology suggesting a parallel growth habit with possible interpenetration twin growths, which is expected in crystal growth from a vapor phase reaction or decomposition. Measurements of the angular crystal faces suggest this boron powder is the low temperature (800°C - 1100°C) α-rhombohedral form.

EDX spectra (AEE -325 mesh B; AEE 1-5 micron Ti + AEE -325 mesh B; AEE 1-5 micron Ti + Callery 320A) all show traces of Fe which was also found in the reaction pressings in the range of 0.2 to 0.4 weight percent. The Al and Si traces in the EDX spectra were also observed in the chemical analysis of selected reaction pressings.

C. Densified Reaction Pressing Evaluation

Chemical analysis by emission spectroscopy, x-ray diffraction analysis, and a battery of physical and mechanical property testing was applied to selected reaction pressings to assess the effects of powder morphologies, average particle sizes, and chemistries on stoichiometric and off-stoichiometric mixes of selected powder combinations.

1. Emission Spectroscopy

Table V summarizes the results of emission spectroscopic analysis for pressings using four powder sources (Alfa -325 mesh Ti, AEE -325 mesh Ti, AEE -325 mesh B, and Callery 320 Å B). It appears that total metal impurities have been retained at the same levels as the input powders, and the iron content is the most significant contaminant, with silicon, aluminum and manganese as secondary contaminants.

## TABLE V

## CHEMICAL ANALYSIS FOR PRESSINGS USING THREE POWDER SOURCES

| POWDER SOURCE | HP187 | HP214 | HP226 |
|---|---|---|---|
| | WT. PERCENT | | |
| TITANIUM | ALFA-325 | AEE-325 | AEE-325 |
| BORON | CALLERY (320Å?) | AEE-325 | CALLERY (320Å?) |
| **ELEMENT** | | | |
| BORON | M | M | M |
| TITANIUM | M | M | M |
| CHROMIUM | 0.004 | 0.02 | 0.004 |
| MANGANESE | 0.12 | 0.06 | 0.02 |
| MAGNESIUM | 0.02 | 0.06 | 0.02 |
| SILICON | 0.08 | 0.12 | 0.10 |
| IRON | 0.2 | 0.4 | 0.4 |
| NICKEL | 0.02 | ND | ND |
| ALUMINUM | 0.12 | 0.08 | 0.06 |
| COPPER | 0.008 | 0.008 | 0.008 |

M = MAJOR
ND = NOT DETECTED

2. X-ray Diffraction

Evaluation of x-ray diffraction traces of reaction pressings is shown in Table VI for two stoichiometric reaction pressings (HP212 and HP226) and in Table VII for two pressings with 7.5% titanium in excess of the stoichiometric composition. All pressings are considered to match the $TiB_2$ ASTM Standard (Card 8-121).

3. Physical and Mechanical Properties

The results of characterization efforts for selected reaction pressings are shown in Table VIII. The initial group of 9 reaction pressings listed in Table VIII explored powder size effects and variation in composition. The final group of 5 reaction pressings represents improvements in hot press processing and powder mixing using powders available in bulk quantities.

The boron powder size effect was examined using nominal powder sizes of 249 μm (-60 mesh), 43 μm (-325 mesh) and Callery 320Å. These powders were combined with two titanium powder sizes, 43 μm (-325 mesh) and 1-5 μm as indicated in Table VIII. Boron carbide as the boron source was examined in the powder size combination of 43 μm Ti with 1-5 μm $B_4C$. Stoichiometric, excess boron (HP228), excess titanium (HP288, 289), and added $TiB_2$ (HP304) compositions were prepared. Jet-mill powder mixing was used for HP303 and HP304; all others were mixed by solids-solids blending.

The reaction pressing of the powder mixes was accomplished in an Astro Industries Inc. Model HP20 3560 Hot Pressing System, equipped with a Honeywell Type RI-3 Small Target Radiamatic Pyrometer for heat-radiation detection and process variable input to the Honeywell Digital Control Programmer (DCP) Model 770211. The microprocessor-based DCP provides the means to store and

TABLE VI

X-RAY DIFFRACTION ANALYSIS FOR PRESSINGS WITH STOICHIOMETRIC POWDER MIX

| HP212* | | | HP226* | | | $TiB_2$ ASTM 8-121 | | |
|---|---|---|---|---|---|---|---|---|
| I | 2θ | d,A | I | 2θ | d,A | d,A | I | hkl |
| 20 | 27.50 | 3.24 | 30 | 27.5 | 3.24 | 3.22 | 20 | 001 |
| 50 | 34.02 | 2.63 | 40 | 34.1 | 2.63 | 2.62 | 60 | 100 |
| 100 | 44.35 | 2.04 | 100 | 44.39 | 2.04 | 2.033 | 100 | 101 |
| 10 | 56.95 | 1.62 | 10 | 56.90 | 1.62 | 1.613 | 14 | 002 |
| 15 | 61.08 | 1.52 | 15 | 61.10 | 1.52 | 1.514 | 20 | 110 |
| 15 | 68.15 | 1.38 | 15 | 68.20 | 1.37 | 1.374 | 16 | 102 |
| 10 | 68.40 | 1.37 | 10 | 68.40 | 1.37 | 1.370 | 10 | 111 |
| | ----- | | 10 | 72.00 | 1.31 | 1.311 | 8 | 200 |
| 10 | 78.65 | 1.22 | 10 | 78.70 | 1.22 | 1.215 | 14 | 201 |
| 10 | 88.40 | 1.11 | 10 | 88.40 | 1.11 | 1.104 | 12 | 112 |
| | ----- | | | ----- | | 1.020 | 12 | 202 |
| 10 | 101.40 | 0.996 | 15 | 101.30 | 0.997 | 0.9956 | 8 | 103 |
| 10 | 108.50 | 0.950 | 10 | 108.70 | 0.949 | 0.9479 | 10 | 211 |

* FROM DIFFRACTOMETER RECORDS - Ni FILTERED Cu RADIATION, λ = 1.54178 A

TABLE VII

X-RAY DIFFRACTION ANALYSIS FOR PRESSINGS WITH EXCESS (7.5%) Ti

| X-RAY DIFFRACTION DATA | | | | | |
|---|---|---|---|---|---|
| HP288* | | | $TiB_2$ ASTM 8-121 | | |
| I | 2θ | d,A | d,A | I | hkl |
| 26 | 27.59 | 3.23 | 3.22 | 20 | 001 |
| 76 | 34.22 | 2.62 | 2.62 | 60 | 100 |
| 100 | 44.49 | 2.04 | 2.033 | 100 | 101 |
| 13 | 56.95 | 1.62 | 1.613 | 14 | 002 |
| 16 | 61.20 | 1.51 | 1.514 | 20 | 110 |
| 13 | 68.08 | 1.377 | 1.374 | 16 | 102 |
| 16 | 68.17 | 1.376 | 1.370 | 10 | 111 |
| | ----------- | | 1.311 | 8 | 200 |
| 16 | 78.75 | 1.22 | 1.215 | 14 | 201 |
| 17 | 88.48 | 1.10 | 1.104 | 12 | 112 |
| 9 | 98.50 | 1.02 | 1.020 | 12 | 202 |
| 8 | 101.20 | 0.998 | 0.9956 | 8 | 103 |
| 12 | 108.95 | 0.947 | 0.9479 | 10 | 211 |

* HP289 ANALYSIS IDENTICAL

AMOUNT OF Ti RETAINED IS BELOW DETECTION LEVEL

# TABLE VIII

## CHARACTERIZATION RESULTS FOR $TiB_2$ BY REACTION PRESSING

| COMPOSITION[1] | HP # | POWDER SOURCE[2] Ti | POWDER SOURCE[2] B | POWDER SOURCE[2] OTHER | DENSITY[3] IMMERSION ($g/cm^3$) | DENSITY[3] THEORETICAL (percent) | MICRO-[4] HARDNESS, VICKERS, ($kg/mm^2$) | FRACTURE[4] TOUGHNESS, INDENTATION ($MN/m^{1.5}$) | GRAIN[6] SIZE ($\mu m$) | FLEXURE[8] STRENGTH ($MN/m^2$, Ksi) |
|---|---|---|---|---|---|---|---|---|---|---|
| Ti + 2B | 226 | AEE -325 | CALL. 320A | --- | 4.15 | 91.7 | 2753 | 4.52 | 3.6 | 192 , 27.9 |
| Ti + 2B | 187 | ALFA -325 | | --- | 4.38 | 96.8 | 2536 | 5.46 | | 569 , 82.5 |
| Ti + 2.04B | 228 | AEE -325 | | --- | 3.88 | 85.7 | 2736 | NBI[5] | 4.7 | 210 , 30.4 |
| Ti + 2B | 214 | | AEE -325 | --- | 4.17 | 92.1 | 1985 | NBI | 5.2 | 249 , 36.1 |
| Ti + 2B | 215 | | ALFA -60 | --- | 4.02 | 88.8 | 2214 | NBI | 3.4 | 226 , 32.7 |
| Ti + 2B | 212 | AEE 1-5 μm | 320A | --- | 4.33 | 95.6 | 2703 | 5.57 | | --- --- |
| Ti + 2B | 213 | | AEE -325 | --- | 4.16 | 91.9 | ---- | ---- | 7.2 | --- --- |
| Ti + 2B | 230 | | ALFA -60 | --- | 4.31 | 95.1 | 2225 | NBI | 5.9 | 339 , 49.2 |
| 2Ti + $B_4C$ | 231 | ALFA -325 | --- | AEE $B_4C$ 1-5 μm | 2.97 | 65.6 | 3239 303 | 2.84 NBI | --- | 59.9, 8.7 |
| Ti + 2B | 284 | AEE -325 | AEE -325 | --- | 4.27 | 94.3 | ---- | ---- | 8.4 | 299 , 43.4 |
| 1.077 Ti + 2B | 288 | | | --- | 4.34 | 96.0 | ---- | ---- | 9.2 | 307 , 44.5 |
| 1.077 Ti + 2B | 289 | | | --- | 4.35 | 96.1 | ---- | ---- | 10.1 | 304 , 44.1 |
| Ti + 2B | 303[7] | | | --- | 4.28 | 95.2 | ---- | ---- | --- | 426 , 61.8 |
| Ti + 2B + 0.001 $TiB_2$ | 304[7] | | | AEE $TiB_2$ 1-5 μm | 4.34 | 96.5 | ---- | ---- | --- | 394 , 57.2 |

(1) STOICHIOMETRY
(2) -325 EQUIVALENT TO 0.0017" (43 μm)
320A = .032 μm
-60 EQUIVALENT TO 0.0098" (249 μm)
(3) THEORETICAL DENSITY = 4.527 $g/cm^3$ (FOR Ti + 2B)
(4) TEST CONDITIONS: MINIMUM: 5 INDENTS AT 0.1 kg
MAXIMUM: 15 INDENTS, UP TO 6 kg
(5) NBI = NOT BY INDENTATION
(6) INTERCEPT METHOD
(7) JET-MILLED POWDER MIX
(8) ROOM TEMPERATURE; 0.7" AND 0.3" SPANS

run set point programs. A graphite die assembly (1.750" ID) with a filament wound "strongback" contains the compact during processing in a furnace atmosphere of flowing $N_2$ and with an applied force of 15000 pounds. Temperature of the hot press die assembly was monitored using the L&N Model 8634-C Precision Optical Pyrometer with accuracy at 1035°C $\pm$ 4°C and at 1760 $\pm$ 8°C.

## III. DISCUSSION

The results of the reaction thermochemistry indicate the adiabatic temperature of 3600°K, obtained in the reaction

$$Ti(s) + 2B(s) \rightarrow TiB_2(s) + \Delta H$$

exceeds the melting point of $TiB_2$, reported as 3063°K (2790°C).[3] Studies of the microstructure of the reaction pressings confirm that a liquid phase is present during the process, and the reaction is in a liquid + $TiB_2$ phase field. Secondary phases (possibly TiB and Ti) and contaminants (Si, Fe, possibly Ti(B,Si), SiC) are rejected from the liquid as the mass cools and are located at pore surfaces and as inclusions in the $TiB_2$ matrix.[4]

The effect of starting powder purity and grain size on microstructure development and on physical and mechanical properties has been difficult to uncover. Stoichiometric and excess Ti powder mixes react to form $TiB_2$ with total metal impurities 0.57 to 0.75%. The formation of a liquid during the reaction is a desirable situation and rapid short term densification is predicted. The reaction is homogeneously auto-nucleated by an externally applied

(3) High Temperature Chemistry of the Binary Compounds of Boron, P.W. Gilles, in Borax to Boranes, Advances in Chemistry Series Number 32, Amer. Chem. Soc. 1961.

(4) "Self-Propagating Reactions for Synthesis of High Temperature Materials," P.D. Zavitsanos and J.F. D'Andrea, AMMRC Final Report, February 1985.

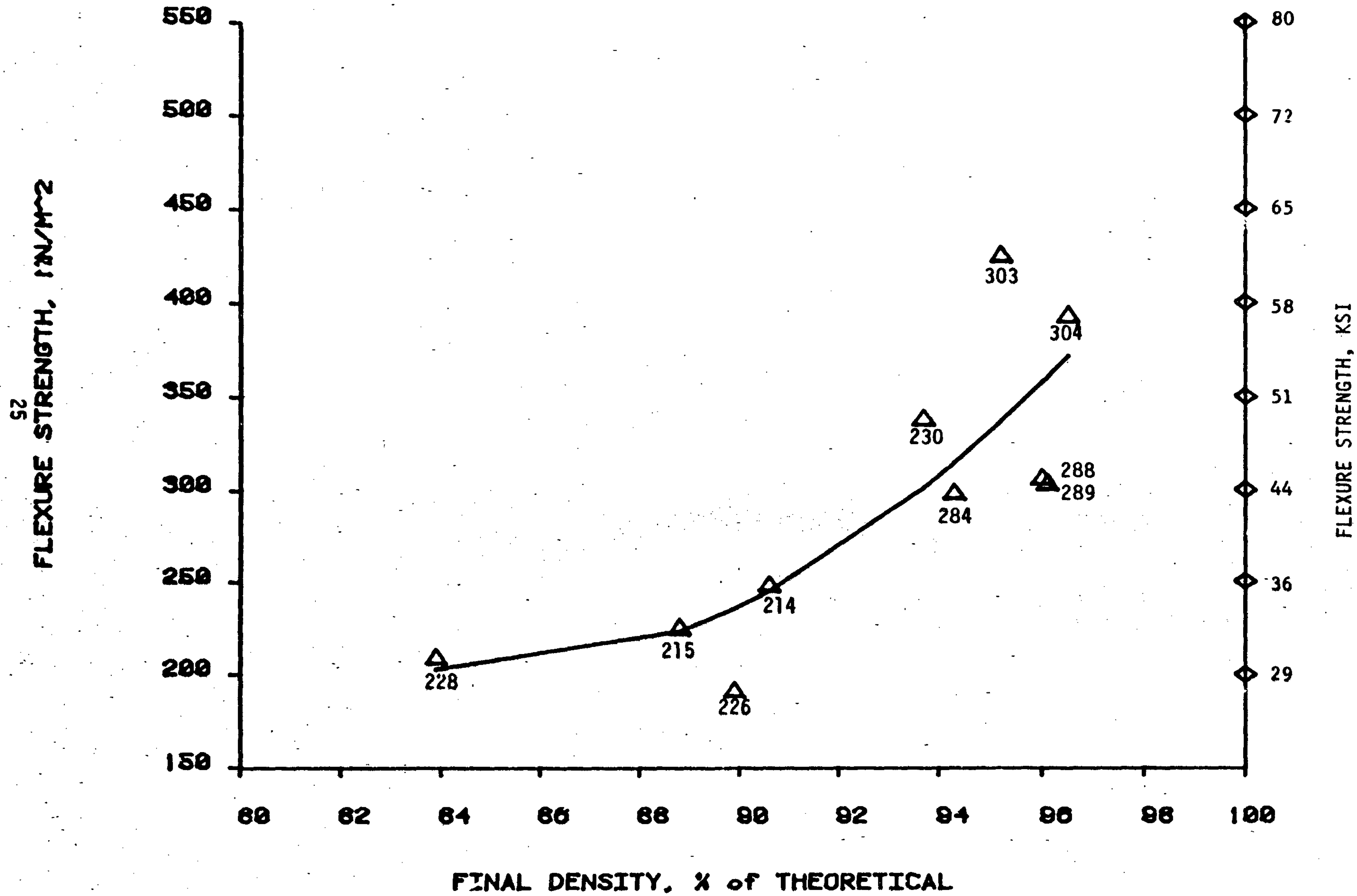
thermal gradient to the maximum process hold temperature of 1760°C. This short-term densification occurs during the auto-ignition of the powder mix at low external process temperatures (700°C to 950°C). The externally-applied process temperature continues to increase after the reaction is complete and the heat of reaction is dissipated. During this post-ignition portion of the processing, sintering densification continues and is controlled by kinetics of particle-particle mass transport or transport through secondary liquid phases as suggested by the microstructure content. The role of secondary phases and contaminants, present as the metal impurities, may be to provide an interparticle liquid phase for the sintering densification that occurs in the post-reaction portion of the process.

Characterization results (Table VIII) indicate mechanical properties (such as flexure strength) are dependent on improvement in final density, Figure 9. The trend of improvement in final density appears to be dependent on improvements in process cycle (continuous external temperature increase versus incremental increases) and changes in powder mixing (jet milling versus solids blending). These process changes have had more effect on properties than powder sources or stoichiometry, with the possible exception of the reaction pressings which used Callery 320Å boron.[5]

The benefit of powder mixing by jet-milling is seen in comparison of the flexure strength of jet-milled HP303, 426 MN/m$^2$ (61.8 ksi) and solids-solids blended HP284, 299 MN/m$^2$ (43.4 ksi). The jet-milling method of fine grinding results in self-attrition of the feed powder mix with essentially

(5) HP212, 226, 228, (a) Microhardness exceeded 2700 Kg/mm$^2$, (b) Fracture toughness measurable by the indentation method. The thin lamellar morphology of the powder suggests a high purity (99.9%) boron source for the Ti + 2B reaction.

Figure 9. EFFECT OF FINAL DENSITY ON FLEXURE STRENGTH



no contamination and has the potential to produce a narrower particle size distribution with a smaller average particle size, and to reduce small particle agglomerates.

## IV. CONCLUSIONS

The heat of the Ti + 2B reaction produces considerable liquid during the process cycle although the relatively fine and uniform grain indicates complete melting is not achieved. This situation is desirable since micro-cracking due to thermal expansion anisotropy in $TiB_2$ is minimized in structures with grain sizes below the critical grain size $\sim$ 15 microns.[6,7]

The reaction appears to proceed by a mechanism which involves the melting of titanium and its movement towards solid boron particles.

Stoichiometric powder mixes, when prepared by jet-milling, produce a significant increase in flexure strength properties in the reaction pressing. Powder mixes with excess Ti (5.0 and 7.5 weight percent) produce $TiB_2$ pressings very similar in properties to stoichiometric mixes when powder preparation was solids-solids blending. However, powder mixes with excess B (2.0 weight percent) were low density (less than 85%) and lower strength than stoichiometric powder mixes.

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(6) Effect of Microstructure on the Properties of $TiB_2$ Ceramics, M.K. Ferber, P.F. Becher, C.F. Finch, Communications of the Amer. Cer. Soc., January 1983.

(7) Sintering and Properties of Titanium Diboride Made from Powder Synthesized in a Plasma-Arc Heater, H.R. Baumgartner and R.A. Steiger, J. Amer. Cer. Soc., Vol. 67, No. 3, March 1984.

Powder characterization was limited to evaluation by SEM/EDX of individual powders and powder mixes and to mass spectrometry of individual powders. This approach was adequate to assess some effects of powder morphology on reaction pressing properties. However, the results of the jet-milling experiment require an improved powder characterization regimen to obtain increased density and mechanical properties and provide a basis for future improvements for this process.

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